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PSEUDOPOLAROGRAPHIC DETERMINATION OF METAL COMPLEX STABILITY CO--ETC(U)

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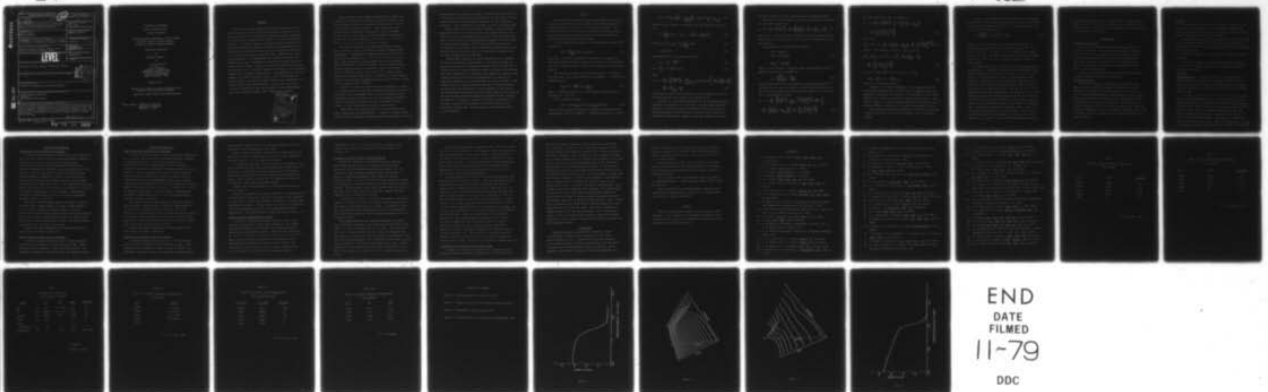
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Pseudopolarographic Determination of Metal Complex
Stability Constants in Dilute Solution
By Rapid Scan Anodic Stripping Voltammetry

Prepared for Publication
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Analytical Chemistry

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ABSTRACT

The theory of anodic stripping voltametry states that at any deposition potential, the deposition current will either be the limiting current or a fraction of the limiting current, depending on the deposition potential with respect to the metal desposition potential. By using a computer controlled anodic stripping voltameter with automatic background correction, pseudopolarograms can be obtained by plotting the peak area vs the deposition potential for a series of stripping voltametric runs. With ASV as a method of amplification, the ligand number and stability constants are determined for metal complexes at concentration ranges expected of natural water systems. Results for lead and cadmium with chloride and carbonate are in excellent agreement with those of less sensitive methods used at higher concentrations. No complexation of lead and cadmium was found with glycine at pH = 4.68. The structure of arsenic (III) at 1.0 ng/ml in acidic solutions was determined to be $\text{As}(\text{OH})_3$ using a gold film electrode. Finally, the speciation of lead in a geothermal water was examined by pseudopolarography and a shift consistent with a PbCl^+ complex was observed.

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The evaluation of the complexing properties of metals in solution has long been of interest to analytical chemists, who have developed a variety of techniques suited to the assignment of metal complexation in solution. These techniques, which include visible absorption spectrometry, isotopic exchange methods, and in a few cases, vibrational (Raman) spectroscopy as well as more exotic methods, have been used by a variety of groups to study the kinetics of ligand exchange.

For dilute solutions, in the millimolar range, however, these techniques lack the sensitivity needed to evaluate metal complexation. Polarographic techniques based on the shift of the half-wave potential ($E_{1/2}$) with ligand concentration were first used by Hevrowsky (1) and Lingane (2,3) to investigate metal complexation in dilute solution; these and similar determinations via ion-selective electrodes (4,5) do not extend to metal concentration ranges below about 10^{-5} M. Thus, neither technique is directly applicable to evaluations of metal complexation at concentrations approximating those found in dilute natural waters, typically 10^{-8} - 10^{-10} M.

In order to extend the sensitivity of polarography, a number of techniques have been employed, including differential pulse (6,7) and square wave polarography (8,9), various alternating current polarography-based techniques (10-12), and stripping voltammetry (13-18), but these techniques have not seen extensive use in studies of metal complexation in dilute natural waters.

Most recent work has been aimed at the classification of metal complexation in natural waters. A number of schemes (13-15) based on anodic stripping voltammetry have been developed to classify

metal complexes as "free" or "bound". Florence (16-18) has devised a system which classifies metal complexes as (1) free ions; (2) ASV labile complexes; (3) dissociable complexes; (4) non dissociable complexes. These systems have been called "coarse" speciation (19).

Direct identification of the metal complex in dilute solution via determination of the ligand number and complex stability constant has only been attempted quite recently, and most studies have used relatively large metal concentrations compared to levels found in dilute natural systems. This "fine" speciation (19) has not involved ASV, because many runs are needed to establish peak shifts, and ASV peak positions are known to be sensitive to factors such as ionic strength and scan rate (20).

Because metal reduction has been demonstrated to be sensitive to metal complexation through changes in the amount of metal deposited as a function of deposition potential (21), coupling reproducible plating at various potentials with a sensitive ASV technique will allow measurements of deposited metal charge (or, here, as peak currents derived from the ASV stripping peak) as a function of deposition potential. Two recent papers use linear scan ASV in this fashion (22,23) to obtain stability constants in dilute solutions. We report here the application of this technique to thin, glassy carbon-supported mercury and gold films using rotating disk electrodes and minicomputer-controlled background subtracted anodic stripping voltammetry. The system is capable of generating automated Q vs. E_d plots, called pseudopolarograms, with either linear scan or staircase stripping ASV. We also describe the theoretical basis of the technique.

THEORY

At any deposition potential E_d , the deposition current $i(t)$ is given by either the limiting current of the deposition process at the rotating disk electrode, or some fraction thereof. For constant plating time, the material deposited also will vary with E_d , and the individual stripping steps will merely analyze the material preconcentrated in the electrode.

For a rotating disk electrode, the instantaneous current $i(t)$ is given by:

$$i(t) = \frac{nFAD_{OX}}{\delta_{OX}} [C_{OX}^o - C_{OX}(0,t)] \quad (1)$$

where C_{OX}^o is the bulk concentration of analyte ion, $C_{OX}(0,t)$ is the surface concentration of analyte ion at time t , δ is the thickness of the diffusion layer, and the other symbols have their usual meaning.

De Vries and Van Dalen (24-26) have shown for thin mercury film electrodes the surface activity of the amalgam as a function of plating time is:

$$C_{RED}(0,t) = \frac{i(t)}{nFA} \left(\frac{t}{l} + \frac{1}{3D_{RED}} \right) \quad (2)$$

Here t is plating time and l is film thickness; this equation is suitable for $t \geq 20$ sec.

For an electrode process

$$i(t) = nFA\{k_{fh}C_{OX}(0,t)\gamma_O - k_{bh}C_{RED}(0,t)\gamma_R\} \quad (3)$$

where k_{fh} and k_{bh} are the forward and backward heterogeneous rate constants for the metal reduction. Combining equations 1-3 yields:

$$i(t) = nFAk_{fh}\gamma_{OX}\left(C_{OX}^o - \frac{i(t)\delta_{OX}}{nFAD_{OX}}\right) - k_{bh}\gamma_r i(t) \left(\frac{t}{l} + \frac{1}{3D_{RED}}\right) \quad (4)$$

Since we desire charge, we integrate (4) with respect to time to get:

$$Q = \frac{k_{fn}\delta_{OX}}{D_{OX}} (Q_{LIM} - Q)\gamma_{OX} - k_{bh}\left(\frac{t}{2l} + \frac{1}{3D_{RED}}\right)Q\gamma_r \quad (5)$$

$$\text{where } Q_{LIM} = \int_0^t i_{LIM} dt = \int_0^t \frac{nFAC_{OX}^o}{\delta_{OX}} D_{OX} dt \quad (6)$$

$$Q = \int_0^t i(t) dt \quad (7)$$

Rearrangement of (5), and substitution of

$$k_{fn} = k_{fh}^o e^{-\frac{\alpha nF}{RT} E_d} \quad (8)$$

$$\text{and } \frac{k_{bh}}{k_{fh}} = \exp\left\{\frac{nF}{RT} (E_d - E^o)\right\} \quad (9)$$

gives

$$E_d - E^o = \frac{RT}{nF} \ln \left[\left(\frac{Q_{LIM} - Q}{Q} \right) - \frac{D_{OX}}{\delta_{OX} k_{fh}^o \gamma_{OX}} \exp(\alpha nF E_d / RT) \right] - \frac{RT}{nF} \ln \left(\frac{\delta_{OX}}{D_{OX}} - \frac{\gamma_{OX}}{\gamma_r} \right) - \frac{RT}{nF} \ln \left(\frac{1}{3D_{RED}} + \frac{t}{2l} \right) \quad (10)$$

where $\alpha(E_d)$ is the transfer coefficient for the reduction and k_f^o is the heterogeneous rate constant for reduction at E^o .

Equation 10 is the general equation for the pseudopolarographic reduction and stripping of a free model ion under quasi-reversible conditions. Various techniques including ASV (27) and stripping chronoamperometry (28) can be used to strip the metal ions out of the fiber and monitor the change, so this and subsequent equations

are left in terms of charge, rather than peak stripping current.

When $k_f^0 \rightarrow \infty$, the reaction at the electrode surface is reversible and equation 10 reduces to:

$$E_d - E^0 = \frac{RT}{nF} \ln \left(\frac{Q_{LIM} - Q}{Q} \right) + \frac{RT}{nF} \ln \left(\frac{\delta_{OX} \gamma_{OX}}{D_{OX} \gamma_{RED}} \right) - \frac{RT}{nF} \ln \left(\frac{1}{3D_{RED}} + \frac{t}{2l} \right) \quad (11)$$

Equation 11 is similar to that obtained by Zirino and Kounaves (29), but differs from their result as we use the exact expression for C_r and integrate.

For complexes, we consider the equilibria:



where complex formation is presumed rapid and reversible, and the stability constant β_j is defined as:

$$\beta_j = \frac{[ML_j^{n+}]}{[M^{n+}][L]^j} \cdot \frac{\gamma_{ML_j}}{\gamma_M \gamma_L^j} \quad (13)$$

Using the method of DeFord and Hume (30), which presumes only M^{n+} is reducible, all $D_{OX} = D$, excess L, and all activity constants do not vary with distance from the electrode, equation 14 is obtained for a quasireversible system:

$$\begin{aligned} E_d = E^0 + \frac{RT}{nF} \ln \left[\left(\frac{Q_{LIM} - Q}{Q} \right) + \frac{D}{k_f^0 \delta_{OX}} \sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_L^j}{\gamma_{ML_j}} \right) e^{\frac{\alpha n F}{RT} E_d} \right] - \\ \frac{RT}{nF} \ln \left[\frac{\gamma_r D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) \right] - \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_L^j}{\gamma_{ML_j}} \right) \right] \end{aligned} \quad (14)$$

For reversible cases, this is reduced to:

$$E_d = E_o + \frac{RT}{nF} \ln \left(\frac{Q_{LIM} - Q}{Q} \right) - \frac{RT}{nF} \ln \frac{\gamma_r^D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) - \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j (L)^j \gamma_i^j}{\gamma_{MLj}} \right) \right] \quad (15)$$

from which:

$$E_{1/2}^*, \text{ comp} = E_o - \frac{RT}{nF} \ln \frac{\gamma_r^D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) - \frac{RT}{nF} \ln \sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_i^j}{\gamma_{MLj}} \right) \quad (16)$$

results. For constant values of l , δ_{OX} , γ_r and t :

$$\Delta E_{1/2}^* = (E_{1/2}^*, \text{ free} - E_{1/2}^*, \text{ comp}) = - \frac{RT}{nF} \ln \left(\frac{D}{D_{OX}} \cdot \gamma_M \right) + \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_i^j}{\gamma_{MLj}} \right) \right] \quad (17)$$

or, for a single complex with $\gamma_M \approx \gamma_{ML}$, $D \approx D_{OX}$

$$\Delta E_{1/2}^* \approx \frac{RT}{nF} \ln \beta_j + j \frac{RT}{nF} \ln a_L \quad (18)$$

where a_L is the ligand activity.

Equation 17 is exactly analogous to that obtained by DeFord and Hume for polarographic reduction of metal complexes where many complexes are possible, and equation 18 is analogous to the Lingane equation (3), suited for analysis of single complex systems. Thus, plots of $\Delta E_{1/2}^*$ vs. A_L provide metal complexation information through analyses similar to those used in classical polarographic studies.

Here, because stripping peak heights are directly proportional to total charge (26), we use ASV peak heights in our evaluations of $E_{1/2}^*$.

Davison has examined (31) the limitations on conventional polarographic and voltammetric schemes used to monitor speciation, and finds for conventional ASV that, for a kinetic current equal to 10% of the limiting current:

$$Q = \frac{\beta^{3/2} [L]}{k_1^{1/2}} (1 + \beta [L])^{1/2} = \frac{9\delta}{D^{1/2}} \quad (17)$$

where k_1 is the second order rate constant for the rate of substitution of the active form of the metal, here M^{n+} . For $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, Q values of $10^4 - 10^6$ result for δ between 10^{-4} and 10^{-2} cm . For ligand concentrations in the 10^{-3} M range, and for $k_1 = 10^9 \text{ l mol}^{-1} \text{ sec}^{-1}$, limiting β values of about 10^5 are obtained.

The same argument can be applied to the pseudopolarographic determination of stability constants, since the technique relies on the measurement of charge passed during the plating period. There are some differences, however. Because plating times should be kept short, to avoid altering the composition of the solution, normal ASV with long plating times cannot be used, as serious metal depletion results. With the ASV method using background subtraction, sensitivities are such that a five minute plating period allows detection of pg/ml levels of metals (27); this allows the observation of small kinetic currents, approximately 1% of the diffusion current in the absence of complexer. The β values easily observable would then extend to about 10^{-6} for ligand concentrations in the 10^{-3} M range. The precision of the determination suffers slightly here, though, with kinetic currents on the order of 1% of the diffusion currents, because

the entire pseudo-polarogram is simply reduced in height proportionally, making the error in determining the half-wave potential somewhat larger. The possibility of decreasing the rotation rate, thus increasing δ , also exists.

EXPERIMENTAL

Equipment and Apparatus

The rapid-scan, background-subtracted ASV apparatus described in reference 27 was used for these studies. Modifications were made to the software to allow a sequence of scans to be performed automatically, with each run differing by a fixed value in the plating potential, but otherwise having identical parameters. Runs were stored sequentially on the disk to allow easy processing.

Measurements of pH were made with a Beckman 4500 digital pH meter, calibrated with pH 4.008 solution.

Electrodes and Cell

Both mercury and gold film electrodes were used in this study, the gold electrode being used for studies of arsenic speciation. Preparation of the electrodes has been discussed (27). A saturated KNO_3 bridge was used between the S.C.E. reference electrode and test solution to avoid contamination of the solution with trace amounts of complexer. The cell (27) was cleaned thoroughly with 5N citric acid between runs to avoid any transfer of complexer. This is particularly necessary in the case of arsenic, as arsenic species strongly absorb on the cell, and later interfere.

Reagents

The standards used in the work reported in reference 27 were also used as standards for this work. Arsenic standards were prepared by dissolving ultrapure As_2O_3 (Alpha) in ultrapure NaHCO_3 (Baker) and adjusting the pH with Ultrex HCl.

Dilute perchloric acid (0.1N) was made by diluting the reagent grade acid (Mallinckrodt) with distilled water. Dilute sodium hydroxide (0.3N) was made from reagent grade pellets (Mallinckrodt) and distilled water.

The ionic strength of all solutions was adjusted with KNO_3 solutions.

Trace metal content of solutions was adjusted by addition of 100 μl of 1-2 $\mu\text{g/ml}$ standards. The transfer was performed with Eppendorf pipettes.

Procedure

Data Acquisition. A series of solutions of ligand were prepared from the stock solution of the ligand. These solutions were spiked to obtain a final trace metal content of 1-5 ng/ml , the ionic strength was adjusted with KNO_3 and the pH with either HClO_4 or NaOH .

A portion (75 ml) of each solution was subjected to analysis by the pseudopolarographic process. This consisted of a five minute deaeration of the solution, with rotation of the preplated electrode, after which a series of ASV experiments were performed on the solution, each at a different plating potential. The ASV run consisted of plating for a specified time, usually 150 sec, at the deposition potential. The potential is switched to the rest potential when 2 seconds remain of plating time. Stirring at a specified rate was performed until 15 seconds of plating time

remained, after which the solution was allowed to become quiescent before the scan. A single scan, using either the linear ramp or staircase waveform, was then performed, using multiple point averaging (typically 16 points). Stirring at the cleaning potential was then performed for 20 sec., after which a 10 sec quiescent period was provided. With 2 seconds remaining, the potential was again switched to the rest potential, and another scan, exactly like the first, was used to monitor the background. Current measurements were subtracted, point by point, and the result was plotted on the Tektronix 4012 screen, and stored on disk. The deposition potential was redefined, and another run was automatically performed, exactly like the first, but at a different deposition potential. This process was continued, until a specified number of runs was performed. The resultant file of ASV runs could be used to generate a pseudopolarogram for each peak present in the voltammogram. A pseudopolarogram run, like that described above, was performed for each solution. The electrode film was maintained between solutions to insure that uniform conditions applied within a series of runs; it was washed with distilled water between analyses of different solutions to prevent carryover of ligand.

Data Reduction. The ASV peak heights were measured with an interactive graphics routine. The plating potentials and peak heights were plotted for each solution, resulting in a series of pseudopolarograms for each metal.

Because, for ASV the peak current is directly proportional to charge stripped, the pseudopolarograms were examined for reversibility by plotting the deposition potential E_d versus $\log [i_L - i/i]$,

where the limiting current, i_L , was estimated from the top of the step-shaped wave, and i was the peak current monitored for the metal of interest on the ASV run where the deposition potential E_d was used. A straight line, with slope of approximately $59.1/n$ mv resulted for a reversible system; non-linear relationships, or slopes drastically different from the $59.1/n$ value expected were treated as irreversible systems.

For reversible systems, the least squares best estimate was used to calculate $E_{1/2}^*$ from $\log [(i_L - i)/i] = 0$. The error in this value is estimated at 1% relative. For irreversible systems, estimates were made of $E_{1/2}^{*irr}$ by extrapolating the foot of the wave upward, estimating the limiting current, and evaluating the potential for a current value equal to one-half the limiting current. The error in this value is somewhat larger, about 3-5% relative.

Values for $E_{1/2}^*$ (or $E_{1/2}^{*irr}$) were then plotted versus the log of ligand concentration, and the slopes of the resultant linear relationships were evaluated via linear regression analysis.

Intercepts were also calculated. The errors in $E_{1/2}^*$ were used to obtain an estimate of the errors in the ligand number, p , and the stability constant, $\log \beta$, calculated from the slope and intercept, respectively. The more exact method of DeFord and Hume (30) as modified by Varga and others (32-33) was not used here, as the scope of such a study (which would require at least 10-20 pseudopolarograms) was beyond this work, whose intent is to demonstrate the feasibility of the technique. Instead, the simpler method of Lingane (2, 3) was used. Future experimentation, involving sufficient runs to use the DeFord and Hume procedure, is planned.

RESULTS AND DISCUSSION

Cadmium and Lead Complexation by Chloride

A series of KCl solutions of fixed 0.10M ionic strength and pH = 5.00 were examined with the pseudopolarographic technique. A staircase scan with $\tau = 10.0$ msec was used in the ASV runs, with 150 sec plating times used for deposition. Twenty ASV experiments, differing in plating potential by 40 mv, were run. The rest potential was -1200 mv (S.C.E.) and the plating potentials ranged from -1000 mv to -200 mv (S.C.E.). Both the Pb and Cd pseudopolarograms were observed to behave reversibly, with slopes from -30 to -33 mv (theoretical -29.8 mv). Table I lists the $E_{1/2}^*$ values obtained for cadmium as a function of chloride concentration. From the table, a least-squares fit gives a ligand number p of 1.1 ± 0.1 and an equilibrium constant of $\log \beta = 3.2 \pm 0.2$.

For lead, shifts were much smaller, as shown in Table II. From the table, a least squares fit gives a ligand number of 0.7 ± 0.2 and a stability constant of $\log \beta = 1.4 \pm 0.3$. Values for the lead-chloride system are much less precise because of the small shifts, combined with the error in locating $E_{1/2}^*$. More ASV runs would better define the curve, and better located $E_{1/2}^*$ values here, resulting in less error.

Results here agree reasonably well with previous literature values, as shown in Table III.

Cadmium and Lead Complexation by Carbonate

A series of Na_2CO_3 solutions at pH = 7.87 were prepared with fixed ionic strength (0.1M) by addition of KNO_3 . Metal concentration was nominally 2 ng/ml for both Cd and Pb. An experiment, identical to the one used for the chloride studies,

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was performed. Neither the Cd, nor the Pb polarogram was totally reversible, slopes being greater than -38mv.

Table IV lists the shifts in the half-wave potential for lead. Using these values, a ligand number of 0.9 ± 0.1 and a stability constant of $\log \beta = 6.1 \pm 0.1$ may be calculated.

It should be noted that a plot of $E_{1/2}^*$ versus $\log [\text{HCO}_3^-]$ also gives a linear relation, with a slope indicating a ligand number of 0.9 as well. Stumm (34) has shown, however, that all reported bicarbonate complexes may be better interpreted as carbonate complexes. Thus, the data reported here are regarded as indicative of carbonate, rather than bicarbonate species.

Results for lead agree quite well with published values, as shown in Table V.

Results for cadmium are listed in Table VI. The observed shifts are quite small, within even the error attributed to the assignment of $E_{1/2}^*$ values. At this pH, cadmium is apparently not significantly complexed by carbonate. Similar results were obtained by differential pulse polarography and ASV of more concentrated Cd-CO_3^{2-} systems (35). CdCO_3 was observed at higher pH values, however (34).

Cadmium and Lead Complexation by Glycine

A series of solutions of glycine, adjusted to pH = 4.68, was made up, again with a total ionic strength of 0.1M. Pseudopolarographic analysis was performed as described previously, using the same conditions as before. Table VII shows the shifts in $E_{1/2}^*$ for Pb and Cd as a function of the glycine concentration. Again, shifts are within the error of the experiment, and no complexation has resulted for either the Pb or the Cd. The interaction of glycine with Pb and Cd has been studied by ASV and DPP analysis of more concentrated solutions, where no

complexation of Cd or Pb was observed (35), although glycine complexes of Cd have been claimed (36), but this work is in question (37).

Structure of Arsenic (III) in Aqueous Solution

Arsenic has received a considerable amount of attention in the past, primarily due to the analytical difficulties associated with its relative insolubility in mercury (38, 39). A variety of electrochemical techniques have been applied in efforts to improve the detection limit values for arsenic analyses (40-46). No concerted effort has been applied to studies of As speciation in dilute solution using electrochemical methods, however. Recent advances in the field, brought about by the use of gold wire (43) or gold film (47) electrodes combined with ASV, suggested that an attempt was feasible.

A solution of As (III) in 0.1M KNO_3 was prepared. The pH was adjusted to a series of values with dilute HClO_4 and dilute NaOH. The nominal As concentration was 1.0 ng/ml. The effects of pH on the $E_{1/2}^*$ value for the As stripping peak on an Au film electrode were briefly investigated by obtaining pseudopolarograms for As at several pH values.

The pseudopolarograms were obtained using 300 sec plating time, followed by background subtracted staircase ASV, with a step height of 3.66mv and a delay time of 16.7 msec. Total scan time was 5 sec. It was observed here that linear scan ASV gave much poorer peaks as well as less effective removal of background, while for other pseudopolarograms, little difference (other than sensitivity) was observed. The same film was used for all runs. Plating potentials varied between -200 ms and +300 mv versus the S.C.E., with a rest potential of -200 mv (S.C.E.). Solution volumes were 75 ml.

A typical pseudopolarogram obtained at pH = 2.85 and 1.0 ng/ml As (III) is shown in Figure 1. The sequence of ASV runs generating this pseudopolarogram is depicted in Figure 2, where the decay in peak height shows along the y axis. The peak potential for the As peak remains constant. A logarithmic analysis of the pseudopolarograms give slopes near those expected for a reversible system (theoretical -19.8 mv); the values observed were -20, -18, -19 and -18 mv for the four pseudopolarograms.

The peak heights for As on Au films drastically decrease with decreasing pOH, as shown in Figure 3. The runs performed in basic solution gave broad, distorted peaks indicating that the As is converted into a highly irreversible form in basic solution. An analysis of runs in acidic solution with data given in Table VIII, gives a ligand number of 3.0 ± 0.1 and an intercept of -548.3 mv. The intercept cannot be converted, as was done before, to a log β value as (1) no $E_{1/2}^*$, free value could be obtained for As (III), and (2) values of D_{As} are certainly not comparable to $D_{As(OH)_3}$, due to the large collection of water molecules expected for the "free" As (III) ion (48). Thus, no convenient route to a stability constant for the complex predicted, $As(OH)_3$, exists. Support for such a complex is found in the Raman spectra of dilute solutions of As_4O_6 ; in acid solutions, the only detectable species is $As(OH)_3$. $As(OH)_2O^-$, $As(OH)O_2^{2-}$ and AsO_3^{3-} also appear in basic solutions (49). Such a result is consistent with the ligand number of 3 in acidic solution, and with the degradation of the As peak in basic solution, as the amount of $As(OH)_3$ decreases.

Estimation of Lead Species in Geothermal Water

A sample of air-exposed geothermal water obtained from the Lawrence Livermore Laboratory, (Department of Energy) project in

the Imperial Valley, California, was filtered under air through a 0.45 μ filter. The pH was 1.99. The pH was adjusted to 5.00, and the filtrate was diluted by a factor of 40 to obtain an approximate ionic strength, mostly as NaCl, of 0.1M. Nominal concentration of minor elements were Pb (7 μ g/ml), Cu (25 ng/ml), Fe (6 μ g/ml) and Sn (1 μ g/ml). A pseudopolarographic scan at low sensitivity was performed, and is plotted for Pb in Figure 4. The half-wave potential, of -501 mv, is consistent with the shift observed above for PbCl^+ in 0.1M KCl at pH = 5.00. It is reasonable to assume that the Pb exists primarily as PbCl^+ in this solution. An attempt was made to examine data for cadmium, but the much larger Pb wave obscured the Cd wave. In view of the high Pb concentration, simple ligands present, and convenient ionic strength, this solution must be regarded as only a model system, and many more ligands and systems must be studied to ascertain direct speciation like that approximated above, but it certainly seems feasible. Work is underway to demonstrate this feasibility in natural systems with metal concentrations in the low ppb range. Thus direct assessment of chemical models (e.g., 50) seems feasible. This is particularly useful in view of the drastically different effects of different complexes in natural systems, especially as regards bioavailability and toxicology (51-53).

CONCLUSIONS

Pseudopolarography has been shown to provide a rapid, sensitive means of performing measurements in very dilute solution (ng/ml or less). Because the theoretical treatment is so closely related to classical polarography, the considerable literature on the polarographic analysis of solutions may be applied to the problem of analysis of pseudopolarographic waves.

Results identical to those obtained by other, less sensitive, means were obtained for the Cd-Cl, Pb-Cl and Pb-CO₃ systems. Cd-CO₃, Cd-glycine and Pb-glycine were found not to interact in the pH ranges studied.

The speciation of As(III) in acid solution was examined using the new technique. The complex As(OH)₃ was identified as the dominant electrochemically-active species, consistent with Raman results.

The speciation of Pb in a geothermal water was examined by pseudopolarography. A shift consistent with a PbCl⁺ complex was observed.

The new technique of pseudopolarography, performed with rapid-scan ASV instrumentation, appears to be a major advance in the area of chemical speciation.

CREDITS

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TABLE 1

SHIFT OF $E_{1/2}^*$ WITH CHLORIDE CONCENTRATION
FOR CADMIUM^a

$E_{1/2}^*$	$[Cl^-]$	$\log [Cl^-]$
-745±5	0.0050	-2.3
-758±5	0.010	-2.0
-775±5	0.050	-1.3
-789±5	0.10	-1.0
-725±5	0	--

^a I = 0.10, pH = 5.00

TABLE II

SHIFT OF $E_{1/2}^*$ WITH CHLORIDE CONCENTRATION
FOR LEAD^a

$E_{1/2}^*$	$[Cl^-]$	$\log [Cl^-]$
-480±5	0.005	-2.3
-485±5	0.01	-2.0
-495±5	0.05	-1.3
-499±5	0.1	-1.0
-475±5	0	--

^a I = 0.10, pH = 5.00

TABLE III

COMPARISON OF RESULTS FOR
CADMIUM AND LEAD CHLORIDE SPECIES

<u>Metal</u>	<u>P</u>	<u>I</u>	<u>log β</u>	<u>Reference</u>
Cd	1	1.0	1.7 - 2.2	54
Cd	1	0.1	3.2	This work
Pb	1	0.1	1.0 - 1.6	54
Pb	1	0.1	1.4	This work

TABLE IV

SHIFT OF $E_{1/2}^*$ WITH CARBONATE CONCENTRATION
FOR LEAD^a

$E_{1/2}^*$	$[\text{HCO}_3^-]$	$\log [\text{CO}_3^{2-}]$	$[\text{CO}_3^{2-}]$
-623±5	5.2×10^{-3}	-1.02	0.095
-595±5	2.6×10^{-3}	-1.3	0.047
-551±5	5.2×10^{-4}	-2.0	0.0095
-545±5	2.6×10^{-4}	-2.3	0.0047
-501±5	0	--	

^a I = 0.1, pH = 7.87

TABLE V
COMPARISON OF RESULTS FOR
LEAD CARBONATE SPECIES

<u>Method</u>	<u>I</u>	<u>Pb</u> ^a	<u>pH</u>	<u>log β</u>	<u>Reference</u>
ASV	0.1	200	7.3 - 10.3	6.4	34
DPP	0.1	200-50	5.0 - 9.1	6.1	34
Polarog.	1.7	20000	10.9	8.2 ^b	55
DPASV	0.1	500	-	6.3	56
Cyclic voltammetry	0.7	10	7.2	6.21	57
Pseudopolog.	0.1	2	7.87	6.1	This work

^a in ng/ml

^b value is log β_2

TABLE VI

SHIFT OF $E_{1/2}^*$ WITH CARBONATE CONCENTRATION
FOR CADMIUM^a

$E_{1/2}^*$	$[\text{CO}_3^{2-}]$
-728±5	5.2×10^{-3}
-722±5	2.5×10^{-3}
-725±5	5.2×10^{-4}
-725±5	2.6×10^{-4}
-720±5	0

^a I = 0.1, pH = 7.87

TABLE VII

SHIFT OF $E_{1/2}^*$ WITH GLYCINE CONCENTRATION
FOR CADMIUM AND LEAD^a

$E_{1/2}^*$ (Cd)	$E_{1/2}^*$ (Pb)	[Glycine]
-720±5	-537±5	.005
-715±5	-539±5	.01
-715±5	-539±5	.05
-715±5	-545±5	.1
-715±5	-537±5	0

^a I = 0.1, pH = 4.68

TABLE VIII

SHIFT OF $E_{1/2}^*$ WITH HYDROXIDE CONCENTRATION
FOR ARSENIC^a

$E_{1/2}^*$	<u>pH</u>	<u>pOH</u>
-42±3	6.65	8.35
-33±2	4.26	9.74
86±1	3.56	10.44
108±1	2.85	11.15

^a I = 0.1M (KNO₃)

CAPTIONS FOR FIGURES

Figure 1: Pseudopolarogram for arsenic on gold.

Figure 2: Sequence of runs used to generate pseudopolarogram.

Figure 3: Dependence of arsenic peak on pOH.

Figure 4: Pseudopolarogram of lead species in geothermal water.

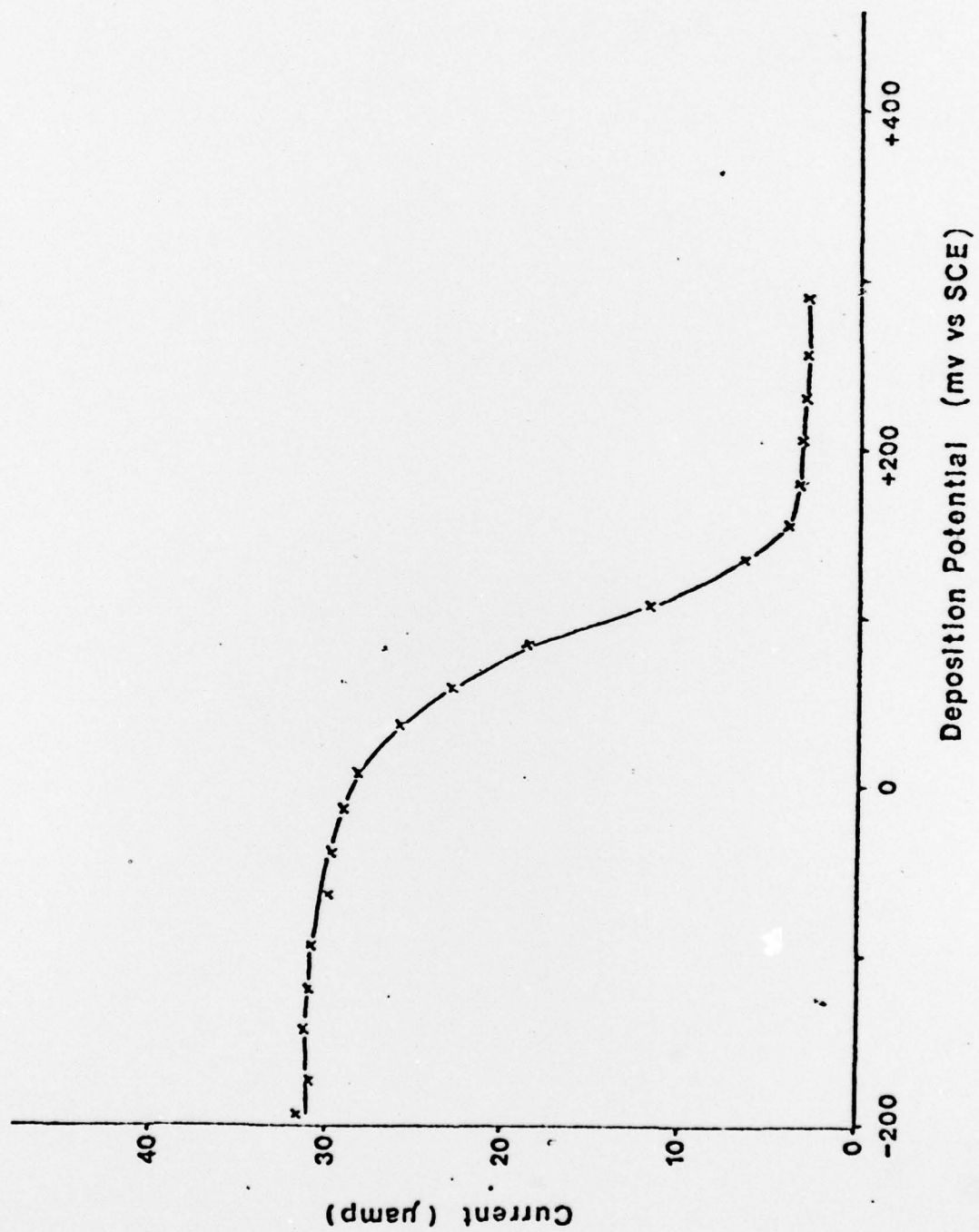


Figure 1

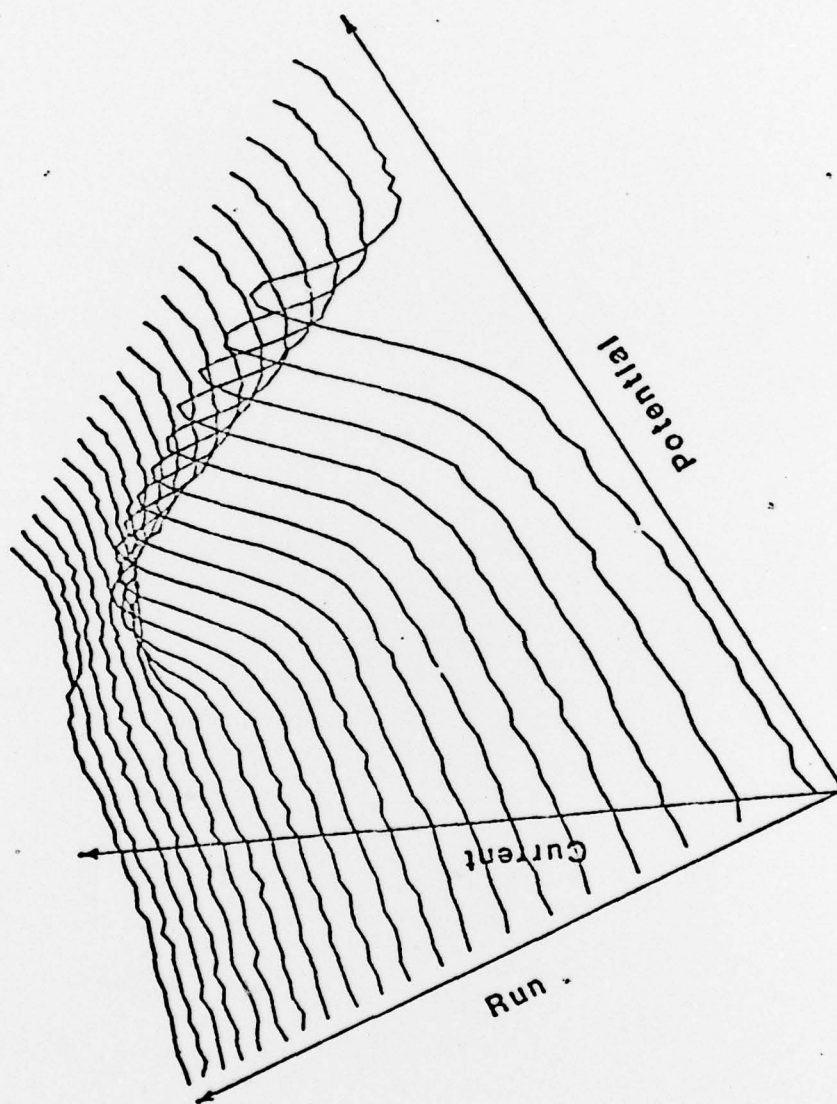


Figure 2

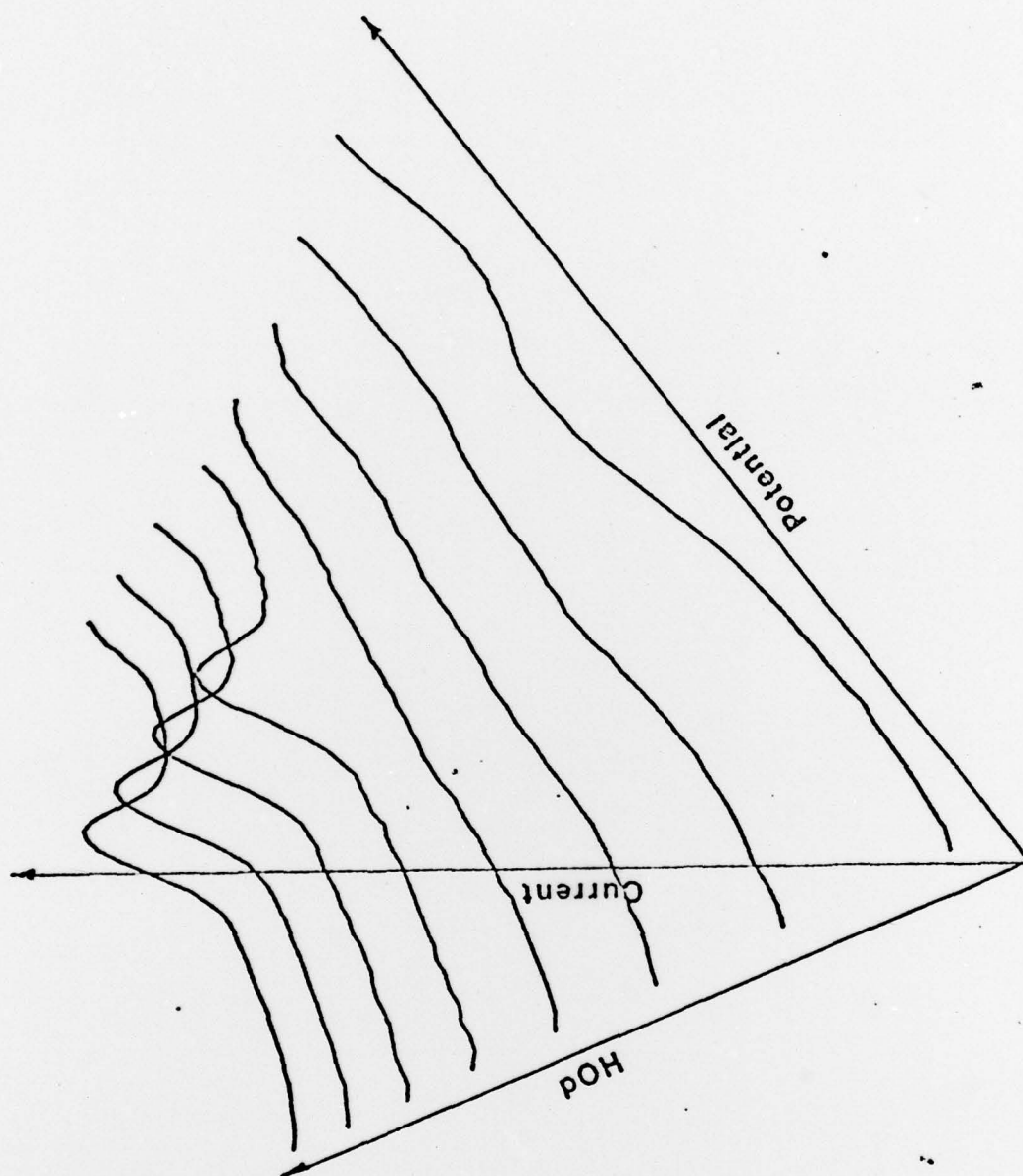


Figure 3

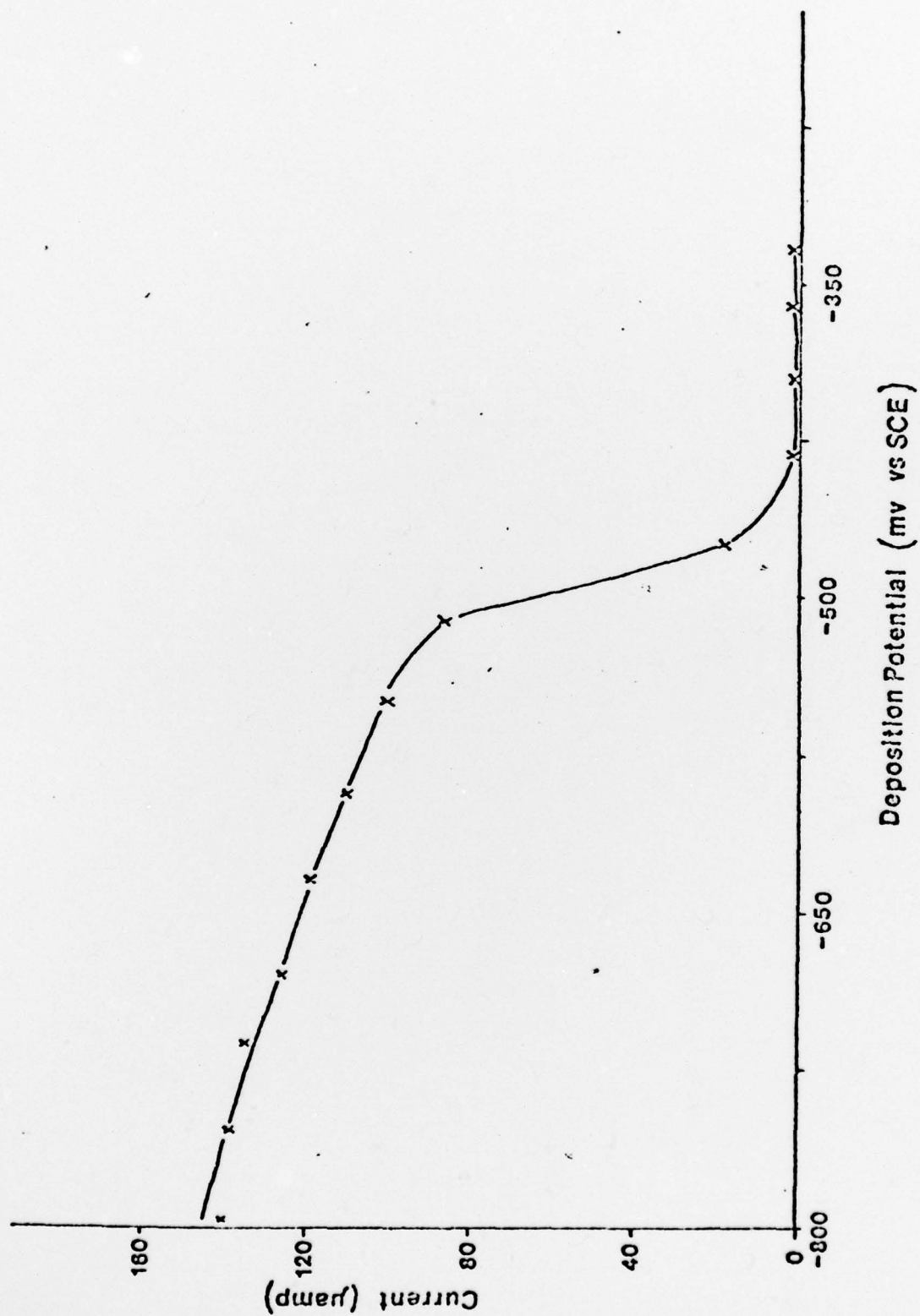


Figure 4